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[19. ABSTRACT]

SYNTHESIS AND CHARACTERIZATION OF NOVEL ALUMINUM-ARSENIC COMPOUNDS II.  
CRYSTAL STRUCTURES OF  $[R_2AlAs(SiMe_3)_2]_2$  ( $R = i\text{-Bu, Me}$ ) AND  $i\text{-Bu}_2(Cl)Al \cdot As(SiMe_3)_3$

R. L. Wells, A. T. McPhail, and T. M. Speer

Department of Chemistry, P. M. Gross Chemical Laboratory  
Duke University Durham, NC 27706

**ABSTRACT.** - The feasibility of utilizing dehalosilylation and lithium chloride elimination reactions for the preparation of compounds that may serve as precursors to aluminum-arsenic containing semiconducting materials has been further investigated. The novel aluminum-arsenic dimers  $[i\text{-Bu}_2AlAs(SiMe_3)_2]_2$ , (1) and  $[Me_2AlAs(SiMe_3)_2]_2$  (2) were prepared by coupling reactions between  $LiAs(SiMe_3)_2$  and  $R_2AlCl$  ( $R = i\text{-Bu}$  and  $Me$ , respectively). Reactions between  $As(SiMe_3)_3$  and  $R_2AlCl$  ( $R = i\text{-Bu, Me}$ ) in 1:1 and 1:2 mole ratio at ambient temperature have failed to give expected dehalosilylation products, but have instead yielded the adducts  $R_2(Cl)Al \cdot As(SiMe_3)_3$  [ $R = i\text{-Bu}$  (3) and  $Me$  (4)]. All compounds were characterized by partial elemental analysis and  $^1H$ ,  $^{13}C\{^1H\}$  and  $^{27}Al\{^1H\}$  NMR spectroscopy. Compounds 1, 2 and 3 were fully characterized by single-crystal X-ray analysis. Crystal data are as follows: 1, monoclinic, space group  $C2/c(C2h^6)$ ,  $a = 19.202(2) \text{ \AA}$ ,  $b = 12.601(1) \text{ \AA}$ ,  $c = 19.278(2) \text{ \AA}$ ,  $\beta = 106.86(1)^\circ$ ; 2, triclinic, space group  $P1(C_i^1)$ ,  $a = 9.723(1) \text{ \AA}$ ,  $b = 9.968(1) \text{ \AA}$ ,  $c = 9.246(1) \text{ \AA}$ ,  $\alpha = 99.18(1)^\circ$ ,  $\beta = 115.70(1)^\circ$ ,  $\gamma = 77.13(1)^\circ$ ; 3, monoclinic, space group  $P2_1/c(C2h^5)$ ,  $a = 15.105(1) \text{ \AA}$ ,  $b = 11.574(1) \text{ \AA}$ ,  $c = 18.655(1) \text{ \AA}$ ,  $\beta = 119.25(1)^\circ$ .

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CRYSTAL STRUCTURES OF  $[R_2AlAs(SiMe_3)_2]_2$  ( $R = i\text{-Bu, Me}$ ) AND  $i\text{-Bu}_2(Cl)Al \cdot As(SiMe_3)_3$

by

R. L. Wells, A. T. McPhail, and T. M. Speer

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Duke University  
Department of Chemistry  
Durham, NC 27706

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**Synthesis and Characterization of  
Novel Aluminum-Arsenic Compounds - II<sup>†</sup>. Crystal Structures of  
[R<sub>2</sub>AlAs(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (R = *i*-Bu, Me) and *i*-Bu<sub>2</sub>(Cl)Al•As(SiMe<sub>3</sub>)<sub>3</sub>.**

**Richard L. Wells\*, Andrew T. McPhail and Timothy M. Speer**

Department of Chemistry, Paul M. Gross Chemical Laboratory, Duke University,  
Durham, NC 27706, U.S.A.

**ABSTRACT.** - The feasibility of utilizing dehalosilylation and lithium chloride elimination reactions for the preparation of compounds that may serve as precursors to aluminum-arsenic containing semiconducting materials has been further investigated. The novel aluminum-arsenic dimers [*i*-Bu<sub>2</sub>AlAs(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (1) and [Me<sub>2</sub>AlAs(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (2) were prepared by coupling reactions between LiAs(SiMe<sub>3</sub>)<sub>2</sub> and R<sub>2</sub>AlCl (R = *i*-Bu and Me, respectively). Reactions between As(SiMe<sub>3</sub>)<sub>3</sub> and R<sub>2</sub>AlCl (R = *i*-Bu, Me) in 1:1 and 1:2 mole ratio at ambient temperature have failed to give expected dehalosilylation products, but have instead yielded the adducts R<sub>2</sub>(Cl)Al•As(SiMe<sub>3</sub>)<sub>3</sub> [R = *i*-Bu (3) and Me (4)]. All compounds were characterized by partial elemental analysis and <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H} and <sup>27</sup>Al{<sup>1</sup>H} NMR spectroscopy. Compounds 1, 2 and 3 were fully characterized by single-crystal X-ray analysis. Crystal data are as follows: 1, monoclinic, space group C2/c(C<sub>2h</sub><sup>6</sup>), *a* = 19.202(2) Å, *b* = 12.601(1) Å, *c* = 19.278(2) Å, β = 106.86(1)°; 2, triclinic, space group P $\bar{1}$ (C<sub>i</sub><sup>1</sup>), *a* = 9.723(1) Å, *b* = 9.968(1) Å, *c* = 9.246(1) Å, α = 99.18(1)°, β = 115.70(1)°, γ = 77.13(1)°; 3, monoclinic, space group P2<sub>1</sub>/c(C<sub>2h</sub><sup>5</sup>), *a* = 15.105(1) Å, *b* = 11.574(1) Å, *c* = 18.655(1) Å, β = 119.25(1)°.

<sup>†</sup>For Part I, see reference 5.

## INTRODUCTION

The groundbreaking work of Beachley and Coates in the mid-1960's utilized alkane elimination reactions between  $\text{Me}_3\text{Al}$  and  $\text{Ph}_2\text{EH}$  ( $\text{E} = \text{P}, \text{As}$ ) to prepare compounds of the type  $[\text{Me}_2\text{AlEPh}_2]_2$  [1,2]. As evidenced by a paucity of related references in the literature, aluminum-arsenic chemistry received little attention following these seminal investigations. In fact, since that time only four dimeric, aluminum-arsenic species have been reported [1,3,4,5]. Therefore, we endeavored to extend the scope of studies in our laboratory to include the preparation of such moieties. To this end, we began to investigate the uses of dehalosilylation and lithium coupling reactions toward the fabrication of aluminum-arsenic dimeric and mixed bridge (i.e., containing core rings of the type  $\text{Al-As-Al-Cl}$ ) species.

Initial results suggest that coupling reactions between  $\text{LiAs}(\text{SiMe}_3)_2$  and  $\text{R}_2\text{AlCl}$  ( $\text{R} = \text{alkyl}$ ) are generally applicable in the formation of the aluminum-arsenic oligomeric species. The novel dimers  $[\text{Me}_2\text{AlAs}(\text{SiMe}_3)_2]_2$  and  $[i\text{-Bu}_2\text{AlAs}(\text{SiMe}_3)_2]_2$  reported herein, as well as the ethyl homolog  $[\text{Et}_2\text{AlAs}(\text{SiMe}_3)_2]_2$  [5] were prepared in our laboratories following this methodology. In fact, the process seems to be applicable to group 13-15 systems in general, as it has been successfully employed to prepare such compounds containing sundry 13-15 combinations with alkyl groups covering a wide range of size [6,7,8].

In systems involving arsenic and some heavier group 13 elements, i.e., Ga and In, dehalosilylation reactions have been shown to be of general utility [8,9,10]. Depending upon reagent stoichiometry employed, such reactions may be enlisted to form mixed bridge or dimeric species. However, contrasting ambient temperature reactions in these systems, the reaction does not proceed between  $\text{As}(\text{SiMe}_3)_3$  and dialkylaluminum chlorides; simple Lewis base adducts are formed. In this way, the adducts  $\text{Me}_2(\text{Cl})\text{Al}\cdot\text{As}(\text{SiMe}_3)_3$  and  $i\text{-Bu}_2(\text{Cl})\text{Al}\cdot\text{As}(\text{SiMe}_3)_3$  were prepared.

## EXPERIMENTAL

### General Considerations.

Tris(trimethylsilyl)arsine and lithium bis(trimethylsilyl)arsenide were prepared by the methods of Becker *et al.* [11]. Diisobutylaluminum chloride was purchased from Strem Chemicals, Inc. and used without further purification. Dimethylaluminum chloride was generously donated by Dr. Gregory H. Robinson, Clemson University and used as received. Other materials, as well as the

manipulative procedures, purification methods, equipment/instruments, and measurement techniques used in this study are described in Part I [5].

#### Preparation of [*i*-Bu<sub>2</sub>AlAs(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (1).

LiAs(SiMe<sub>3</sub>)<sub>2</sub> (0.273 g, 1.55 mmol) was dissolved in the top bulb of a two-bulb reaction flask in 10 mL THF and 30 mL pentane. *i*-Bu<sub>2</sub>AlCl (0.353 g, 1.55 mmol) was dissolved in 35 mL pentane in the bottom bulb, equipped with a magnetic stir bar, and was cooled to -78 °C in an acetone/dry ice bath. The top bulb of the reaction vessel was cooled with a liquid nitrogen wand. LiAs(SiMe<sub>3</sub>)<sub>2</sub> was added over 15 minutes and a white precipitate formed. The solution was stirred for 1 d at -78 °C and allowed to warm slowly to room temperature. Volatiles were removed *in vacuo* and 75 mL pentane was syringed onto the resulting off-white solid. The solution was filtered *via* cannula to a round-bottomed flask. Volatiles were removed *in vacuo* to leave a white solid that was recrystallized from pentane at -15 °C to give **1** (0.335 g, 73% yield), mp 243 °C. Analysis of the precipitate showed that 0.061 g (93% theoretical) of LiCl was eliminated over the course of the reaction. Anal. Calcd. (Found) for C<sub>28</sub>H<sub>72</sub>Al<sub>2</sub>As<sub>2</sub>Si<sub>4</sub>: C 46.39 (46.02), H 9.94 (9.89). <sup>1</sup>H NMR: δ 2.19 (m, CH, 4H), 1.25 (d, (CH<sub>3</sub>)<sub>2</sub>CH, 24H), 0.66 (d, CH<sub>2</sub>, 8H), 0.49 (s, Si(CH<sub>3</sub>)<sub>3</sub>, 36H). <sup>13</sup>C{<sup>1</sup>H} NMR: δ 28.44 (s, (CH<sub>3</sub>)<sub>2</sub>CH), 27.72 (s, CH), 4.83 (s, Si(CH<sub>3</sub>)<sub>3</sub>), CH<sub>2</sub> resonance not observed. <sup>27</sup>Al{<sup>1</sup>H} NMR: δ 61.63 (br s).

Preparation of [Me<sub>2</sub>AlAs(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (2). LiAs(SiMe<sub>3</sub>)<sub>2</sub> (0.338 g, 1.48 mmol) was dissolved in 10 mL THF and 30 mL toluene in the top bulb of a two-bulb reaction flask. Me<sub>2</sub>AlCl (0.137 g, 1.48 mmol) was dissolved in the bottom bulb, equipped with a magnetic stir bar, in 40 mL toluene and cooled to -78 °C in an acetone/dry ice bath. LiAs(SiMe<sub>3</sub>)<sub>2</sub> was added to the bottom bulb dropwise, over ten minutes with formation of a white precipitate. The solution was stirred overnight at -78 °C and allowed to warm slowly to room temperature. The solution was filtered *via* cannula to a round-bottomed flask. Volatiles were removed *in vacuo* to leave an off-white solid that was recrystallized from pentane at -15 °C to give **2** (0.284 g, 69% yield), mp 184 °C. Analysis of the precipitate revealed that 0.063 g LiCl (95% theoretical) were eliminated over the course of the reaction. Anal. Calcd. (Found) for C<sub>16</sub>H<sub>48</sub>Al<sub>2</sub>As<sub>2</sub>Si<sub>4</sub>: C 34.52 (34.39), H 8.69 (8.85). <sup>1</sup>H NMR: δ 0.40 (s, Si(CH<sub>3</sub>)<sub>3</sub>, 36H), -0.03 (s, CH<sub>3</sub>, 12H). <sup>13</sup>C{<sup>1</sup>H} NMR:

$\delta$  4.513 (s, Si(CH<sub>3</sub>)<sub>3</sub>), CH<sub>3</sub> resonance not observed. <sup>27</sup>Al{<sup>1</sup>H} NMR:  $\delta$  176.51 (br s).

#### Preparation of *i*-Bu<sub>2</sub>(Cl)Al•As(SiMe<sub>3</sub>)<sub>3</sub> (3).

(a) *Reaction of i-Bu<sub>2</sub>AlCl with As(SiMe<sub>3</sub>)<sub>3</sub> (1:1 mole ratio).* As(SiMe<sub>3</sub>)<sub>3</sub> (0.589 g, 2.00 mmol) in 25 mL pentane was added to *i*-Bu<sub>2</sub>AlCl (0.354 g, 2.00 mmol) in 30 mL pentane in a one-necked, round-bottomed reaction flask equipped with a magnetic stir bar and fitted with a Teflon valve. No color change or precipitate formation was noted upon addition. The solution was stirred for 2 d at RT and volatiles were removed *in vacuo* to leave a white solid that was recrystallized from pentane at -15 °C to give 3 (0.922 g, 97.9% yield), mp 157 °C. No Me<sub>3</sub>SiCl was eliminated over the course of the reaction. Anal. Calcd. (Found) for C<sub>17</sub>H<sub>45</sub>AlAsClSi<sub>3</sub>: C 43.30 (43.04), H 9.63 (9.65), Cl 7.52 (7.41). <sup>1</sup>H NMR:  $\delta$  2.34 (m, CH, 2H), 1.31 (d, (CH<sub>3</sub>)<sub>2</sub>CH, 12H), 0.50 (d, CH<sub>2</sub>, 4H), 0.31 (s, Si(CH<sub>3</sub>)<sub>3</sub>, 27H). <sup>13</sup>C{<sup>1</sup>H} NMR:  $\delta$  28.58 (s, (CH<sub>3</sub>)<sub>2</sub>CH), 26.99 (s, CH), 3.108 (s, Si(CH<sub>3</sub>)<sub>3</sub>), CH<sub>2</sub> resonance not observed. <sup>27</sup>Al{<sup>1</sup>H} NMR: 182.66 (br s). (b) *Reaction of i-Bu<sub>2</sub>AlCl with As(SiMe<sub>3</sub>)<sub>3</sub> (2:1 mole ratio).* *i*-Bu<sub>2</sub>AlCl (0.380 g, 2.15 mmol) in 25 mL pentane was added to As(SiMe<sub>3</sub>)<sub>3</sub> (0.317 g, 1.08 mmol) in 30 mL pentane in a one-necked, round-bottomed flask equipped with a magnetic stir bar and fitted with a Teflon valve. No color change or precipitation was noticed upon mixing. Following stirring for 3 d at room temperature, volatiles were removed *in vacuo* to leave an off-white solid which was recrystallized from pentane at -15 °C to give clear crystals (0.501 g, 98.4% yield); mp and NMR spectra (<sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H}) matched those of an authentic sample of 3, *vide supra*. No Me<sub>3</sub>SiCl was eliminated over the course of the reaction.

#### Preparation of Me<sub>2</sub>(Cl)Al•As(SiMe<sub>3</sub>)<sub>3</sub> (4).

(a) *Reaction of Me<sub>2</sub>AlCl with As(SiMe<sub>3</sub>)<sub>3</sub> (1:1 mole ratio).* As(SiMe<sub>3</sub>)<sub>3</sub> (0.603 g, 2.05 mmol) in 30 mL pentane was added to Me<sub>2</sub>AlCl (0.189 g, 2.05 mmol) in 35 mL pentane in a one-necked, round-bottomed reaction flask equipped with a magnetic stir bar and fitted with a Teflon valve. Similarly, no precipitate formation or color change was noted upon addition. The solution was stirred for 2 d at RT and volatiles were removed *in vacuo* to leave a white solid that was recrystallized from pentane at -15 °C to give 4 (0.779 g, 98.2% yield), mp 122 °C. No Me<sub>3</sub>SiCl was eliminated over the course of the reaction. Anal. Calcd. (Found) for

$C_{11}H_{33}AlAsClSi_3$ : C 34.14 (33.85), H 8.59 (8.28), Cl 9.16 (8.97).  $^1H$  NMR:  $\delta$  0.28 (s,  $Si(CH_3)_3$ , 27H), -0.08 (s,  $CH_3$ , 6H).  $^{13}C\{^1H\}$  NMR:  $\delta$  2.85 (s,  $Si(CH_3)_3$ ),  $CH_3$  resonance not observed.  $^{27}Al\{^1H\}$  NMR:  $\delta$  166.63 (br s). (b) *Reaction of  $Me_2AlCl$  with  $As(SiMe_3)_3$  (2:1 mole ratio)*.  $Me_2AlCl$  (0.239 g, 2.58 mmoles) in 20 mL pentane were added to  $As(SiMe_3)_3$  (0.380 g, 1.29 mmoles) in 35 mL pentane in a one-necked, round-bottomed flask equipped with a magnetic stir bar and fitted with a Teflon valve. No color change or precipitate formation was seen upon mixing. Volatile reaction products were removed, following stirring at room temperature for 3 d, to leave an off-white solid that was recrystallized from pentane at  $-15\ ^\circ C$  (0.490 g, 98.2% yield); mp and NMR spectra ( $^1H$  and  $^{13}C\{^1H\}$ ) matched those of an authentic sample of **4**, *vide supra*. No  $Me_3SiCl$  was eliminated over the course of reaction.

#### **Attempted Conversion of **1** to $i-Bu_2AlAs(SiMe_3)_2Al(i-Bu)_2Cl$ .**

$i-Bu_2AlCl$  (0.0466 g, 0.264 mmoles) in 25 mL pentane was added to  $[i-Bu_2AlAs(SiMe_3)_2]_2$  (0.0956 g, 0.132 mmoles) in a one-necked, round-bottomed flask fitted with a Teflon valve and equipped with a magnetic stir bar. No color change or precipitate formation was seen upon addition. The solution was stirred for 2 d at RT and volatiles were removed *in vacuo* to leave a white solid that was recrystallized from pentane at  $-15\ ^\circ C$  to give colorless, clear crystals.  $^1H$  and  $^{13}C\{^1H\}$  NMR spectra, as well as melting point data, matched those of an authentic sample of **1**, *vide supra*.

#### **Attempted Conversion of **2** to $Me_2AlAs(SiMe_3)_2Al(Me)_2Cl$ .**

$Me_2AlCl$  (0.0364 g, 0.394 mmoles) in 20 mL pentane was added to  $[Me_2AlAs(SiMe_3)_2]_2$  (0.1097 g, 0.197 mmoles) in a one-necked, round-bottomed flask equipped with a magnetic stir bar and fitted with a Teflon valve. No color change or precipitation was noted upon mixing. Following stirring for 1 d at ambient temperature, volatiles were removed *in vacuo* to leave an off-white solid that was recrystallized from pentane at  $-15\ ^\circ C$  to give clear, cubic crystals; NMR spectra ( $^1H$  and  $^{13}C\{^1H\}$ ) and mp matched those of an authentic sample of **2**, *vide supra*.



### Attempted Internal Dehalosilylation of 3 and 4.

An NMR tube sample of  $R_2(Cl)Al \cdot As(SiMe_3)_3$  ( $R = i\text{-Bu, Me}$ ) in benzene- $d_6$  was heated in an oil bath at 87 °C for 4 d.  $^1H$  NMR spectra taken periodically over this time showed that no internal dehalosilylation or decomposition had occurred.

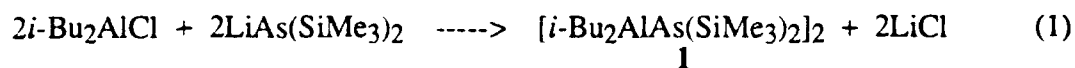
### Structural Analyses of 1, 2 and 3.

Crystals of 1, 2 and 3 used for X-ray analysis were obtained by recrystallization from pentane at -15 °C and sealed inside thin-walled glass capillaries under an argon atmosphere. Crystallographic data and data collection parameters are summarized in Table I. Intensity data were corrected for the usual Lorentz and polarization effects; empirical absorption corrections were also applied. The crystal structure of 1 was solved by direct methods (MULTAN 11/82). Approximate non-hydrogen atom coordinates were derived in part from an  $E$ -map and from subsequent difference Fourier syntheses phased by an increasing number of atoms. The heavy-atom approach was used to solve the crystal structures of 2 and 3 for which initial arsenic atom coordinates were derived from Patterson maps. The remaining non-hydrogen atoms were located in a series of weighted  $F_o$  and difference Fourier syntheses. Several rounds of full-matrix least-squares refinement of non-hydrogen atom positional and thermal parameters (at first isotropic, then anisotropic) followed in all cases. In the later iterations, hydrogen atoms were incorporated at their calculated positions and an extinction correction was added as a variable. Final difference Fourier syntheses showed no unusual features. For all structure-factor calculations, neutral atom scattering factors and their anomalous dispersion corrections were taken from reference 12. Non-hydrogen atom fractional coordinates and equivalent isotropic thermal parameters for 1, 2 and 3 are listed in Table II.

## DISCUSSION

### Synthesis and Characterization of $[i\text{-Bu}_2AlAs(SiMe_3)_2]_2$ (1).

Reaction of  $i\text{-Bu}_2AlCl$  with  $LiAs(SiMe_3)_2$  in 1:1 molar stoichiometry in pentane at -78 °C affords 1. Compound 1 may be obtained as colorless, cubic crystals in



73% yield by recrystallization from pentane at -15 °C. However, when reaction is

carried out at ambient temperature yield is very low and an uncharacterized, viscous, orange liquid is obtained.  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{27}\text{Al}$  NMR spectroscopic data are consistent with the solid-state structure of **1** as elucidated by single-crystal X-ray analysis. The  $^1\text{H}$  NMR spectrum is comprised of resonances that may be assigned to *i*-Bu groups [(m,  $\delta$  2.19), (d,  $\delta$  1.25), (d,  $\delta$  0.66)] and  $\text{SiMe}_3$  groups (s,  $\delta$  0.49), with requisite integration intensities.

A desirable feature for compounds that may serve as single-source precursors to AlAs is a  $\beta$ -hydrogen source. Such a site may, upon heating, enable  $\beta$ -hydrogen shift with concurrent alkene elimination. The resulting hydridic species may then undergo internal condensation to afford AlAs. With this in mind, decomposition of **1** to AlAs, by several methods, was attempted. In the first, **1** was heated at 110  $^\circ\text{C}$  in refluxing toluene for 7 days. Product analysis (mp,  $^1\text{H}$  and  $^{13}\text{C}$  NMR) showed that no decomposition occurred at this relatively low temperature. Secondly, **1** was heated neat under vacuum in a cool flame. In this instance, sublimation occurred, with no AlAs formation. Product was analyzed by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy and all data were consistent with those of an authentic sample of **1** (*vide supra*). While these initial attempts failed to give the desired product, other means of decomposition are being explored and will be reported in future correspondence.

It has been shown for other Group 13-15 systems, that the dimeric species may be converted to a mixed bridge compound by treatment with two mole equivalents of  $\text{R}_2\text{MCl}$  (M = Group 13). This method has been applied to the preparation of numerous gallium-arsenic compounds [13,14], as well as some indium-arsenic compounds [10]. In an attempt to synthesize analogous aluminum-arsenic containing molecules, **1** was reacted with two mole equivalents of  $i\text{-Bu}_2\text{AlCl}$ . The solution was stirred for two days at room temperature. Analysis of the isolated product demonstrated that no reaction had taken place.

Compound **1** crystallizes in the monoclinic system, space group  $C2/c$ , with four discrete dimers in the unit cell. An ORTEP diagram showing the structure and solid-state conformation is presented in Figure 1. The As atoms lie on a crystallographic  $C_2$  symmetry axis and, accordingly, the Al-As-Al-As ring is required to be strictly planar as was the situation in  $[\text{Et}_2\text{AlAs}(\text{SiMe}_3)_2]_2$  (**5**) which was recently fully characterized in our laboratory [5]. Selected bond lengths and angles are listed in Table III.

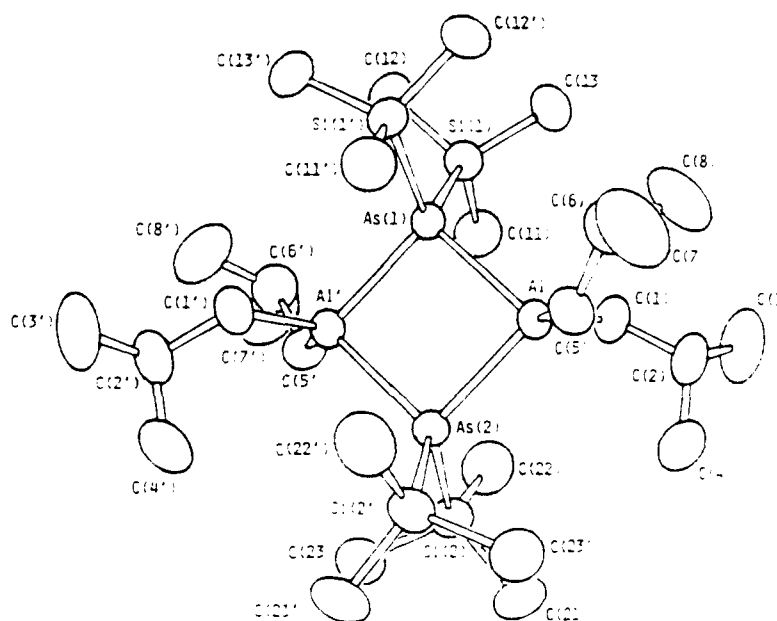
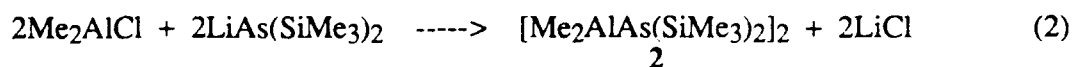


Fig 1. ORTEP diagram (40% probability ellipsoids) of the solid-state structure of (*i*-Bu<sub>2</sub>AlAs(SiMe<sub>3</sub>)<sub>2</sub>)<sub>2</sub> (**1**); primed atoms are related to the unprimed atoms by a crystallographic C<sub>2</sub> symmetry axis passing through the As atoms. Hydrogen atoms have been omitted for clarity.

#### Synthesis and Characterization of [Me<sub>2</sub>AlAs(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (**2**).

Reaction of Me<sub>2</sub>AlCl with LiAs(SiMe<sub>3</sub>)<sub>2</sub> in 1:1 reagent stoichiometry in toluene at -78 °C yields **2**. Product may be isolated in 69% yield by recrystallization from



pentane at -15 °C. Spectroscopic data correspond to the solid-state structure as determined by single-crystal X-ray analysis. The <sup>1</sup>H NMR spectrum is very simple, consisting of resonances that may be assigned to Me groups (s, δ -0.03) and SiMe<sub>3</sub> groups (s, δ 0.40) with integration intensities consistent with structural stoichiometry. In addition, <sup>13</sup>C and <sup>27</sup>Al spectra comprise peaks consistent with this structure. As is true for compound **1**, when reaction is carried out at ambient temperature, yield is very low, the major product being a viscous, orange, uncharacterized liquid.

Compound **2** was allowed to react with two mole equivalents of Me<sub>2</sub>AlCl, in an attempt to form the methyl mixed bridge molecule. After two days, product was isolated and characterized. NMR spectra, as well as melting point, matched those of an authentic sample of **2**. Thus, as was the case for compound **1**, it was not

possible to convert the dimeric species to the mixed bridge under these relatively mild reaction conditions.

Crystals of dimer **2** belong to the triclinic system, space group  $P\bar{1}$ , with the one molecule in the unit cell sitting on a crystallographic center of symmetry and thus, in common with **1** and **5**, the Al-As-Al-As ring is constrained to be planar. An ORTEP diagram for **2** is provided in Figure 2. Selected bond lengths and angles are listed in Table III.

The mean Al-As distances in **2** (2.536 Å) and **1** (2.550 Å) are similar not only to each other but also to the mean of 2.535 Å in **5**, as are the As-Si mean lengths [2.345 Å in **2**, 2.352 Å in **1**, 2.349 Å in **5**]. The mean Al-C distances in **2** (1.965 Å) and **1** (1.980 Å) are not significantly different from the corresponding mean in **5** (1.976 Å). In **2**, **1**, and **5**, the geometry about the Al and As atoms is distorted tetrahedral with the endocyclic angle subtended at As being consistently larger than that at Al [91.71(3)° and 88.29(4)°, respectively, in **2**; corresponding values: mean 92.23°, 87.77(3)° in **1**, and 91.01(5)°, 88.99(5)° in **5**]. Their Si-As-Si angles [108.09(3)° in **2**, mean 105.61° in **1**, 107.59(6)° in **5**] are consistently smaller than tetrahedral while the C-Al-C angles [115.0(2)°, 118.8(2)°, and 115.0(3)° in **2**, **1**, and **5**, respectively] are always larger than tetrahedral.

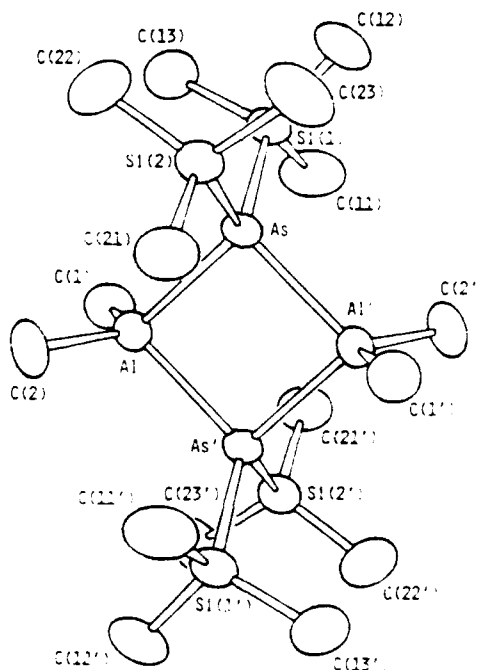
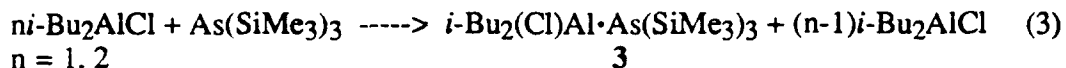


Fig 2. ORTEP diagram (40% probability ellipsoids) of the solid-state structure of  $(\text{Me}_2\text{AlAs}(\text{SiMe}_3)_2)_2$  (**2**); primed atoms are related to the unprimed atoms by a crystallographic center of symmetry. Hydrogen atoms have been omitted for clarity.

### Synthesis and Characterization of $i\text{-Bu}_2(\text{Cl})\text{Al}\cdot\text{As}(\text{SiMe}_3)_3$ (**3**).

Reaction of  $i\text{-Bu}_2\text{AlCl}$  with  $\text{As}(\text{SiMe}_3)_3$  in either 1:1 or 2:1 mole ratio at ambient temperature gives **3**. Product may be obtained in quantitative yield by recrystallizing



from pentane at  $-15^\circ\text{C}$ . All spectroscopic data (including  $^{13}\text{C}$  and  $^{27}\text{Al}$  NMR spectra) are consistent with the solid-state structure as derived from single-crystal X-ray analysis. Thus, its  $^1\text{H}$  NMR spectrum is composed of resonances that may be assigned to  $i\text{-Bu}$  groups [(m,  $\delta$  2.34), (d,  $\delta$  1.31), (d,  $\delta$  0.50)] and  $\text{SiMe}_3$  groups (s,  $\delta$  0.31) with consistent integration intensities.

Compound **3** possesses the necessary traits to undergo internal dehalosilylation, i.e., a chlorine atom on the metal and a  $\text{SiMe}_3$  group on the pnictide. It was thought that **3**, upon heating, would eliminate  $\text{Me}_3\text{SiCl}$  to give **1**. Toward this end, an NMR tube sample of **3** in benzene- $d_6$  was heated in an oil bath at  $87^\circ\text{C}$ . Reaction was monitored by  $^1\text{H}$  NMR spectroscopy and it was found that no such reaction occurred, even after four days.

It has been shown by us, that the adduct  $\text{Cl}_3\text{Al}\cdot\text{As}(\text{SiMe}_3)_3$  when heated neat under vacuum in a cool flame undergoes internal dehalosilylation to give  $\text{AlAs}$  [15]. This methodology does not apply in the case of **3**. Instead, sublimation was seen when **3** was treated in this manner.

Compound **3** crystallizes in the monoclinic system, space group  $P2_1/c$ , with molecules occupying each of the four general positions. An ORTEP diagram illustrating the structure and solid-state conformation is reproduced in Figure 3; selected bond distances and angles are listed in Table III. The staggered conformation around the central Al-As bond in **3** is similar to that around the Ga-As bond in  $(\text{Me}_3\text{CCH}_2)_2\text{Ga}(\text{Cl})\cdot\text{As}(\text{SiMe}_3)_3$  (**6**) [14] [mean rotation from an eclipsed orientation of Al and As substituents is  $36.9^\circ$  in **3** versus  $38.2^\circ$  for the Ga and As substituents in **6**] as are the bonding geometries at these centers [mean  $\text{Si-As-Si} = 107.4^\circ < \text{mean Al-As-Si} = 111.5^\circ$ , mean of the  $\text{Cl-Al-C}$  and  $\text{C-Al-C}$  angles =  $114.8^\circ$  in **3**; corresponding values for **6** are  $106.1^\circ$ ,  $112.7^\circ$ ,  $116.4^\circ$ ]. The Al-As bond in **3** [ $2.573(1) \text{ \AA}$ ] is slightly longer than the mean Al-As distance in **1** ( $2.550 \text{ \AA}$ ), whereas the mean Al-C distance [ $1.972 \text{ \AA}$ ] is essentially equal to that of  $1.980 \text{ \AA}$  in dimer **1**. A parallel situation holds for adduct (**6**) and dimer [ $(\text{Me}_3\text{CCH}_2)_2\text{GaAs}(\text{SiMe}_3)_2$ ]<sub>3</sub> (**7**) [14] where the Ga-As distance in the former [ $2.626(1) \text{ \AA}$ ] is greater than the mean [ $2.587 \text{ \AA}$ ] in the latter while their mean Ga-C

distances [1.997 Å] are identical. The mean As-Si bond length in **3** [2.369 Å] is slightly longer than that of 2.352 Å in **1**.

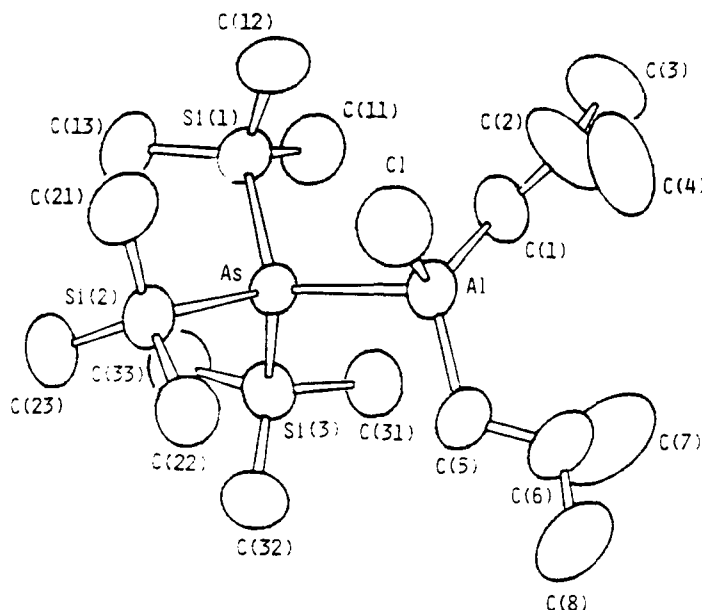


Fig. 3. ORTEP diagram (50% probability ellipsoids) of the solid-state structure of  $i\text{-Bu}_2(\text{Cl})\text{Al}\cdot\text{As}(\text{SiMe}_3)_3$  (**3**). Hydrogen atoms have been omitted for clarity.

### Synthesis and Characterization of $\text{Me}_2(\text{Cl})\text{Al}\cdot\text{As}(\text{SiMe}_3)_3$ (4).

Reaction of  $\text{Me}_2\text{AlCl}$  with  $\text{As}(\text{SiMe}_3)_3$  in pentane in either 1:1 or 2:1 mole ratio at room temperature affords **4**, which may be recovered in quantitative yield by

$$\begin{array}{l} n \text{ Me}_2\text{AlCl} + \text{As}(\text{SiMe}_3)_3 \text{ -----} \rightarrow \text{Me}_2(\text{Cl})\text{Al} \cdot \underset{\text{4}}{\text{As}(\text{SiMe}_3)_3} + (n-1)\text{Me}_2\text{AlCl} \quad (4) \\ n = 1, 2 \end{array}$$

recrystallization from pentane at -15 °C. While crystals of **4** suitable for single-crystal X-ray analysis have not been isolated, other data support the postulation of its structure as an aluminum-arsenic adduct. The <sup>1</sup>H, <sup>13</sup>C and <sup>27</sup>Al NMR spectra suggest such a postulation in that the <sup>1</sup>H integration and splitting patterns are compliant, the <sup>13</sup>C spectrum is appropriate for those peaks observed and the <sup>27</sup>Al NMR spectrum shows that only one type of aluminum is present in the compound. This, coupled with a consistent partial elemental analysis (C, H and Cl), the fact that no Me<sub>3</sub>SiCl was found in reaction volatiles and that yield was quantitative, indicates that the structure of the product is correctly formulated as **4**.

The possibility for **4** to undergo intramolecular dehalosilylation was investigated by heating its NMR tube sample in an oil bath at 87 °C and monitoring any reaction by <sup>1</sup>H NMR spectroscopy. The results showed that no reaction or decomposition occurred, even after four days of such treatment.

## CONCLUSIONS

The work presented here forms a foundation upon which future studies may be built. It appears that dehalosilylation reactions, while employed successfully in systems with heavier metals, do not proceed between tris(trimethylsilyl)arsine and dialkyl aluminum chlorides in the manner anticipated. Instead, simple Lewis base adducts are formed. However, by increasing the temperature of reaction, silyl cleavage may be seen. Lithium coupling reactions between lithium bis(trimethylsilyl)arsenide and dialkyl aluminum chlorides seem to be of general utility in the formation of oligomeric aluminum-arsenic compounds, at least for fairly small alkyl groups. This reaction scheme has been employed to prepare such species with substituents ranging in size from methyl to *iso*-butyl. However, as substituent size increases, the reaction may become sluggish or even cease to be a viable synthetic tool. These, and other matters, will be addressed in future publications.

TABLE I. Crystallographic Data and Measurements<sup>a</sup> for *i*-Bu<sub>2</sub>AlAs(SiMe<sub>3</sub>)<sub>2</sub> (1), [Me<sub>2</sub>AlAs(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (2) and *i*-Bu<sub>2</sub>(Cl)Al•As(SiMe<sub>3</sub>)<sub>3</sub> (3)

	1	2	3
molecular formula	C <sub>28</sub> H <sub>72</sub> Al <sub>2</sub> As <sub>2</sub> Si <sub>4</sub>	C <sub>16</sub> H <sub>48</sub> Al <sub>2</sub> As <sub>2</sub> Si <sub>4</sub>	C <sub>17</sub> H <sub>45</sub> AlAsClSi <sub>3</sub>
formula weight	725.04	556.71	471.16
crystal system	monoclinic	triclinic	monoclinic
space group	C2/c(C <sub>2h</sub> <sup>6</sup> )	P $\bar{1}$ (C <sub>i</sub> <sup>1</sup> )	P2 <sub>1</sub> /c(C <sub>2h</sub> <sup>5</sup> )
<i>a</i> , Å	19.202(2)	9.723(1)	15.105(1)
<i>b</i> , Å	12.601(1)	9.968(1)	11.574(1)
<i>c</i> , Å	19.278(2)	9.246(1)	18.655(1)
$\alpha$ , deg	90.00(-)	99.18(1)	90.00(-)
$\beta$ , deg	106.86(1)	115.70(1)	119.25(1)
$\gamma$ , deg	90.00(-)	77.13(1)	90.00(-)
no. of orient. refls;			
$\theta$ deg, range	25; 36-40	25; 36-40	25; 36-40
<i>V</i> , Å <sup>3</sup>	4464(2)	785.2(3)	2845.5(9)
<i>Z</i>	4	1	4
<i>D</i> <sub>calcd</sub> , g cm <sup>-3</sup>	1.079	1.177	1.100
temp, °C	23	23	23
crystal dimensions, mm	0.36 x 0.40 x 0.40	0.30 x 0.30 x 0.32	0.22 x 0.30 x 0.34
<i>T</i> <sub>max</sub> : <i>T</i> <sub>min</sub>	1.00:0.87	1.00:0.93	1.00:0.70
radiation (wavelength)	Cu-K $\alpha$ (1.5418 Å)	Cu-K $\alpha$ (1.5418 Å)	Cu-K $\alpha$ (1.5418 Å)
$\mu$ , cm <sup>-1</sup>	34.0	47.0	40.3
scan type	$\omega$ -2 $\theta$	$\omega$ -2 $\theta$	$\omega$ -2 $\theta$
scan width, deg	0.80 + 0.14tan $\theta$	0.80 + 0.14tan $\theta$	0.70 + 0.14tan $\theta$
$\theta$ <sub>max</sub> , deg	75	75	75
intensity control	10 6 9, 14 0 10,	1 3 7, 2 6 4,	3 2 1, 2 1 4,
reflxs	1 7 10, 8 8 1	4 2 7, 5 5 1	1 1 5, 1 2 3
variation; repeat time, h	<1%; 2	<1%; 2	<1%; 2
no rflxs recorded	4726 (+ <i>h</i> ,+ <i>k</i> ,± <i>l</i> )	3423 (+ <i>h</i> ,± <i>k</i> ,± <i>l</i> )	6077(+ <i>h</i> ,+ <i>k</i> ,± <i>l</i> )
no rflxs reind, <i>I</i> >3.0 $\sigma$ ( <i>I</i> )	3625	2927	3629
no parameters refined	165	110	209
extinction correction	1.3(1) x 10 <sup>-6</sup>	1.47(4) x 10 <sup>-5</sup>	2.25(5) x 10 <sup>-6</sup>
<i>R</i> , <i>R</i> <sub>w</sub> <sup>b</sup>	0.038, 0.056	0.037, 0.059	0.045, 0.065
goodness-of-fit <sup>c</sup>	1.81	2.13	1.58
max shift;esd in final			
least-squares cycle	0.01	0.02	0.02
final $\Delta\rho$ (e/Å <sup>3</sup> ) max; min	0.40; -0.30	0.56; -0.72	0.39; -0.54

<sup>a</sup>An Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator was used for all measurements. Crystallographic calculations were performed on PDP11/44 and MicroVAX computers by use of the Enraf-Nonius Structure Determination Package (SDP).

<sup>b</sup> $R = \sum |F_o| - |F_c| / \sum |F_o|$ ;  $R_w = [\sum w (|F_o| - |F_c|)^2 / \sum w |F_o|^2]^{1/2}$ ;  $\Sigma w \Delta^2 [w = 1/\sigma^2(|F_o|)]$ ,  $\Delta = (|F_o| - |F_c|)$  was minimized.

<sup>c</sup>Goodness-of-fit =  $[\Sigma w \Delta^2 / (N_{\text{observations}} - N_{\text{parameters}})]^{1/2}$ .



TABLE II. Non-hydrogen Atom Fractional Coordinates and Equivalent Isotropic Thermal Parameters for 1, 2, and 3, with Estimated Standard Deviations in Parentheses

**Compound 1**

Atom	x	y	z	$B_{eq}(\text{\AA}^2)$
As(1)	0.00000(-) <sup>a</sup>	0.14867(3)	0.25000(-) <sup>a</sup>	3.61(1)
As(2)	0.00000(-) <sup>a</sup>	0.42925(3)	0.25000(-) <sup>a</sup>	3.94(1)
Al	-0.01876(4)	0.28818(6)	0.33823(4)	3.86(1)
Si(1)	-0.10187(4)	0.03741(7)	0.20962(5)	4.79(2)
Si(2)	-0.09717(6)	0.54365(7)	0.19450(5)	5.58(2)
C(11)	-0.1814(2)	0.1219(3)	0.1644(2)	6.7(1)
C(12)	-0.0857(2)	-0.0652(3)	0.1451(2)	6.9(1)
C(13)	-0.1201(2)	-0.0324(3)	0.2877(2)	6.6(1)
C(21)	-0.1052(3)	0.6548(3)	0.2559(2)	8.2(1)
C(22)	-0.1834(2)	0.4672(4)	0.1681(3)	8.2(1)
C(23)	-0.0816(3)	0.6020(3)	0.1112(2)	7.7(1)
C(1)	-0.1198(2)	0.2752(3)	0.3439(2)	5.3(1)
C(2)	-0.1386(2)	0.3329(3)	0.4061(2)	6.0(1)
C(3)	-0.2133(2)	0.3062(5)	0.4107(3)	10.5(2)
C(4)	-0.1315(3)	0.4511(4)	0.4000(2)	8.8(1)
C(5)	0.0618(2)	0.2975(2)	0.4293(2)	5.2(1)
C(6)	0.0816(2)	0.2008(3)	0.4783(2)	6.4(1)
C(7)	0.1480(3)	0.2225(5)	0.5429(3)	11.0(2)
C(8)	0.0215(3)	0.1564(4)	0.5025(3)	9.9(1)

<sup>a</sup>Fixed by symmetry

**Compound 2**

Atom	x	y	z	$B_{eq}(\text{\AA}^2)$
As	0.12951(3)	-0.15882(3)	0.03104(3)	3.25(1)
Al	0.1402(1)	0.0799(1)	-0.0220(1)	3.72(2)
Si(1)	0.1584(1)	-0.3269(1)	-0.1670(1)	4.18(2)
Si(2)	0.3168(1)	-0.2298(1)	0.2826(1)	4.31(2)
C(1)	0.1444(4)	0.0825(4)	-0.2319(4)	5.86(8)
C(2)	0.2982(4)	0.1689(4)	0.1600(5)	6.3(1)
C(11)	-0.0064(6)	-0.2890(5)	-0.3634(5)	7.8(1)
C(12)	0.1667(5)	-0.5025(4)	-0.1134(5)	7.0(1)
C(13)	0.3416(5)	-0.3250(5)	-0.1839(5)	7.6(1)
C(21)	0.3011(5)	-0.0917(5)	0.4376(4)	6.2(1)
C(22)	0.5130(5)	-0.2571(6)	0.2871(6)	7.7(1)
C(23)	0.2805(7)	-0.3917(5)	0.3287(5)	8.1(1)

**Compound 3**

Atom	x	y	z	$B_{eq}(\text{\AA}^2)$
As	0.25151(3)	0.18861(4)	0.26823(3)	4.20(1)
Al	0.28913(10)	0.40645(12)	0.27601(8)	5.09(3)
Si(1)	0.27549(10)	0.11766(12)	0.39547(7)	5.86(3)
Si(2)	0.36168(9)	0.08096(12)	0.23584(8)	5.65(3)
Si(3)	0.08267(10)	0.14601(13)	0.16877(9)	5.75(3)
Cl	0.45315(9)	0.39892(15)	0.32837(10)	8.04(4)
C(1)	0.2509(4)	0.4688(5)	0.3552(3)	6.8(1)
C(2)	0.3080(6)	0.5581(7)	0.4134(4)	12.1(2)
C(3)	0.2708(6)	0.5873(8)	0.4750(4)	11.8(2)
C(4)	0.3607(6)	0.6440(6)	0.3980(6)	12.8(3)

TABLE II. (continued)

C(5)	0.2262(5)	0.4581(5)	0.1604(3)	7.7(2)
C(6)	0.2049(5)	0.5844(6)	0.1430(4)	8.9(2)
C(7)	0.1162(7)	0.6211(10)	0.1466(6)	16.2(3)
C(8)	0.1890(7)	0.6169(8)	0.0596(5)	15.0(3)
C(11)	0.1672(4)	0.1651(6)	0.4099(3)	8.6(2)
C(12)	0.3978(5)	0.1799(6)	0.4776(4)	8.5(2)
C(13)	0.2835(5)	-0.0428(5)	0.3983(4)	8.8(2)
C(21)	0.4878(4)	0.0716(6)	0.3313(4)	8.3(2)
C(22)	0.3730(4)	0.1636(5)	0.1556(3)	7.3(1)
C(23)	0.3079(4)	-0.0662(5)	0.1988(3)	7.7(1)
C(31)	0.0028(4)	0.2593(6)	0.1800(4)	7.6(2)
C(32)	0.0722(5)	0.1551(6)	0.0650(4)	7.9(2)
C(33)	0.0442(4)	-0.0009(6)	0.1850(4)	8.3(2)

TABLE III. Selected Bond Distances (Å) and Angles (deg) for 1, 2, and 3, with Estimated Standard Deviations in Parentheses

Compound 1

## (a) Bond Lengths

As(1)-Al	2.543(1)	As(2)-Al	2.557(1)
As(1)-Si(1)	2.348(1)	As(2)-Si(2)	2.355(1)
Al-C(1)	1.981(4)	Al-C(5)	1.978(3)

## (b) Bond Angles

Al-As(1)-Al'	92.55(3)	Al-As(1)-Si(1)	111.62(3)
Al-As(1)-Si(1')	117.19(3)	Si(1)-As(1)-Si(1')	106.69(3)
Al-As(2)-Al'	91.91(3)	Al-As(2)-Si(2)	118.81(3)
Al-As(2)-Si(2')	111.67(3)	Si(2)-As(2)-Si(2')	104.52(4)
As(1)-Al-As(2)	87.77(3)	As(1)-Al-C(1)	108.1(1)
As(1)-Al-C(5)	114.1(1)	As(2)-Al-C(1)	115.0(1)
As(2)-Al-C(5)	108.9(1)	C(1)-Al-C(5)	118.8(2)

Compound 2

## (a) Bond Lengths

As-Al	2.538(1)	As-Al'	2.533(1)
As-Si(1)	2.344(1)	As-Si(2)	2.346(1)
Al-C(1)	1.963(4)	Al-C(2)	1.967(4)

## (b) Bond Angles

Al-As-Al'	91.71(3)	Al-As-Si(1)	112.15(4)
Al-As-Si(2)	113.16(3)	Si(1)-As-Si(2)	108.09(3)
Si(1)-As-Al'	117.46(3)	Si(2)-As-Al'	113.66(4)
As-Al-C(1)	112.1(1)	As-Al-C(2)	113.1(1)
As-Al-As'	88.29(4)	C(1)-Al-C(2)	115.0(2)
C(1)-Al-As'	112.4(1)	C(2)-Al-As'	113.1(1)

TABLE III (continued)

**Compound 3****(a) Bond Lengths**

As-Al	2.573(1)	As-Si(1)	2.366(2)
As-Si(2)	2.381(2)	As-Si(3)	2.359(1)
Al-Cl	2.176(2)	Al-C(1)	1.967(7)
Al-C(5)	1.977(5)		

**(b) Bond Angles**

Al-As-Si(1)	111.23(5)	Al-As-Si(2)	111.38(6)
Al-As-Si(3)	111.92(5)	Si(1)-As-Si(2)	106.83(5)
Si(1)-As-Si(3)	107.05(6)	Si(2)-As-Si(3)	108.18(5)
As-Al-Cl	99.07(7)	As-Al-C(1)	105.3(2)
As-Al-C(5)	105.0(2)	Cl-Al-C(1)	111.4(2)
Cl-Al-C(5)	109.7(2)	C(1)-Al-C(5)	123.2(3)

**(c) Torsion Angles<sup>a</sup>**

Si(1)-As-Al-Cl	83.5(1)	Si(1)-As-Al-C(1)	-31.8(2)
Si(2)-As-Al-C(5)	77.8(3)	Si(2)-As-Al-Cl	-35.5(1)
Si(3)-As-Al-C(1)	87.9(2)	Si(3)-As-Al-C(5)	-43.5(3)

<sup>a</sup>The torsion angle A-B-C-D is defined as positive if, when viewed along the B-C bond, atom A must be rotated clockwise to eclipse atom D.

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**Supplementary Materials Available:** Tables of hydrogen atom coordinates and isotropic thermal parameters, anisotropic temperature factors, complete lists of interatomic distances and angles, including torsion angles for **1**, **2** and **3**, and equations of least-squares planes through groups of atoms for **1** and **2** (6, 5, and 5 pages, respectively); a listing of observed and calculated structure amplitudes for **1**, **2** and **3** (25, 20, and 25 pages, respectively).

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